Catalytica Energy Systems (formerly Catalytica, Inc.)

# Development of Improved Catalysts Using Nanometer-Scale Technology

*In 1994, eight percent of the U.S. gross domestic product was attributed to the chemical and petroleum-refining industries, which produce gasoline, lubricants, diesel fuel, polymers, plastics, and chemical intermediates and products. Of particular concern in these industries was the efficiency of catalysts in a manufacturing process. Catalysts control and enhance the speed of chemical reactions. Improvements in catalyst efficiency could increase product yields, decrease waste byproducts, and potentially lower energy consumption associated with a given process. Catalytica, Inc. and Microfluidics International Corporation formed a joint venture to address this issue. Potential spillover applications of the improved catalysts could benefit the biotechnology, pharmaceuticals, cosmetics, chemicals, coatings, electronics, and food industries. As small companies, Catalytica and Microfluidics alone could analyze only a few catalyst applications by measuring their outcomes. Understanding how a new manufacturing approach could improve catalysts required comprehensively studying the reaction parameters, such as solution concentrations, solution feed rates, and level of acidity or alkalinity. This could only be done with outside funding.*

*Catalytica and Microfluidics applied to the Advanced Technology Program (ATP) in 1994 and were awarded cost-shared funds in order to complete a three-year study of a new process concept to improve catalyst manufacturing. Beginning in 1995, the two companies worked with collaborators and subcontractors, which included several major chemical and petroleum manufacturers, to test the concepts. The companies developed and patented a new catalyst production reactor, called a Multiple Stream Mixer/Reactor (MMR), which produced solid catalyst materials that were more efficient and shared knowledge through publications and presentations. However, the technology was sometimes incompatible with customers' existing manufacturing methods, and Catalytica (later renamed Catalytica Energy Systems) abandoned the technology in 1999 due to lack of funding for continued development. Microfluidics continued developing the MMR and commercialized it in 2004 for laboratory-scale use. Future commercial potential will focus on manufacturing phase-pure, uniform nanomaterials in diverse applications, such as pharmaceuticals, superconductors, pigments, and ceramics. The company anticipates it will have an industrial production model ready for the market by 2005 or 2006.*

**COMPOSITE PERFORMANCE SCORE**

(based on a four star rating)

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**Research and data for Status Report 94-01-0190 were collected during October-November 2004.**

## Catalyst Inefficiencies Result in Waste

The chemical and petroleum-refining industries produce gasoline, lubricants, diesel fuel, plastics, and chemical intermediates and related products. The fuels produced are essential to heat our buildings and to operate the nation's cars, trucks, buses, aircraft, trains, and boats. Other petroleum-derived products are used in antifreeze, tires, cleaning products, cosmetics, polymers, and plastics. In 1993, these industries generated global annual sales of more than $400 billion, with one-third from U.S. manufacturing and sales. This accounted for approximately eight percent of the U.S. gross domestic product.

Catalysts are a key element in the processes used to manufacture many chemical and petroleum products. They control and enhance the speed of chemical reactions by using small amounts of a stable substance, such as metal oxide, which remains unchanged at the end of the reaction. Catalysts enhance the speed of the chemical reaction to transform one chemical into a useful new chemical, a process called conversion. The use of commercial catalysts in production began in 1936, and since then, the industry has adopted many processes, using hundreds of catalysts to increase efficiency in producing fuels and chemicals (John S. Magee and Geoffrey E. Dolbear, *Petroleum Catalysis in Nontechnical Language,* 1998). In most conventional chemical reactors, inadequate mixing and conversion rates can limit the value and performance of a chemical reaction. As a result, product yields are sub-optimal, and unwanted by-products are produced, resulting in higher costs. Improving catalysts is often a key to more efficient chemical reactions.

## Catalytica Proposes to Manufacture More Active Catalysts

Catalytica, Inc. and Microfluidics International Corporation formed a joint venture in 1994 and submitted a proposal to ATP, seeking cost-shared funding to pursue improved catalyst manufacturing. The Catalytica team proposed to collaborate with a subcontractor, Worcester Polytechnic Institute, to develop more active catalysts, which would increase the product-manufacturing rate and/or achieve higher product quality. A more selective catalyst would produce fewer by-products as well as improve raw material utilization, optimize energy efficiency, and reduce purification and disposal costs.

One approach to improving the efficiency was to reduce the catalyst's particle size. Reducing particle size provides increased surface area, which speeds the chemical reaction, because more sites on the particle become available to promote the desired chemical reaction. For example, consider a cube of sugar that is approximately 1.6 cm on each side (or about 2.5 $cm^2$ surface area on each of the six faces of the cube). The total surface area of the powdered sugar cubes is increased to about 2,500 $cm^2$, larger than a standard newspaper page. Similarly, greater catalyst surface area increases the potential reaction rate.

## Team Proposes to Use Microfluidizer

One form of catalyst manufacturing involves a catalyst emulsion (with the consistency of whipping cream) that is pumped through a nozzle and sprayed into a large tank swept with hot air. The water in the emulsion evaporates quickly and solid catalyst particles fall to the bottom of the tank. The technical details of forming these precipitating solids are complex; they include managing solution feed concentrations, solution feed rates, temperature, and solution pH range (degree of alkalinity or acidity). Successful catalysts are generally made from mixtures of elements, usually a metal, metal oxide, or metal sulfide that catalyzes a desired reaction. Small amounts of other elements are added to further improve desired reaction rates. These additives are called promoters (to speed up desired reactions) or poisons (to slow down undesired reactions that produce waste).

Catalytica and Microfluidics proposed to use an existing instrument called a Microfluidizer to produce catalyst precursors in a crystallized form. These precursors could be produced in sizes ranging from 5 to 50 nanometers (a nanometer is 1/1000 of a micrometer). The two companies believed that using the Microfluidizer would result in catalysts that have greater chemical purity and structural uniformity. The Microfluidizer had already been used to emulsify liquids, disperse solids, de-agglomerate particles (split them apart), and rupture biological cell membranes. At the time, Catalytica and Microfluidics researchers believed that similar results could be obtained to improve manufacturing of catalysts for oil and chemical refining.

## Project Success Could Lead to Increased Energy Efficiency and Cost Savings

If successful, the technical advances from this project would also change the processing infrastructure from the traditional large mixing tanks to smaller units with lower capital costs, resulting in reduced catalyst manufacturing costs. Catalysts with greater purity and uniformity would have higher selectivity and conversion rates when used in chemical reactions. If catalyst selectivity (the ability to promote the desired reaction) could be enhanced, then purification, waste, and disposal costs could be reduced, and energy efficiency and resource use could be optimized. For example, in a typical commodity chemical plant that produces 200 million pounds of product per year, a five percent improvement in selectivity would reduce waste emissions by 10 million pounds per year and save several million dollars annually in raw materials and fuel costs.

Catalytica and Microfluidics faced significant risks. On their own they would be limited to addressing a few catalyst opportunities by focusing on proprietary problems defined by a limited set of clients, with fewer chances of a more enabling technical success. ATP support would allow a comprehensive process analysis. Learning to understand and manipulate the processes would be essential to extending and optimizing the technology for catalyst precursor preparation and understanding the impacts of catalyst structure on catalyst performance. ATP awarded the joint venture partners cost-shared funding as part of a general competition in 1994, and the project began in 1995.

## Project Team Develops a New Reactor

The Microfluidizer, a mechanical device initially developed by Arthur D. Little, Inc. worked by combining two chemical solutions, forming two streams of the premixed solutions, and forcing the streams to collide and mix under high speed, pressure, and shear (particles in the solutions hitting each other repeatedly at different angles with each collision). The result was uniform nanometer-scale precipitated solid particles. However, after Catalytica and Microfluidics started testing, they discovered that some of the synthesis methods used by catalyst manufacturers proved to be incompatible with the Microfluidizer.

Furthermore, as researchers pursued this technology, they found an unexpected problem. The Microfluidizer allowed the solutions to make contact before entering the reaction chamber, which caused the reaction to begin too soon. The Microfluidizer was able to produce good texture, distribution, and uniformity, but it was not efficient at controlling the chemistry. Solutions began precipitating before entering the chamber, and some of the desired high-speed, high-shear impact was lost.

Catalytica and Microfluidics proposed to pursue development of a new mixer/reactor that would keep the solution streams separate until they entered the reaction chamber. The new reactor could apply intense mixing to the precipitate-forming reaction itself, not before, thereby permitting fast, controlled, continuous reaction chemistries. The reactor would allow the development and manufacture of nanomaterials. The two solutions would enter the inlet, pass through high-shear microchannels under high pressure, and collide in an intense energy field. Company researchers predicted that resulting materials with nanometer-scale dimensions would have smaller crystallite size (affording more surface area), improved homogeneity, and greater chemical purity. Developing the mixer/reactor became an important focus of the project.

## Researchers Target Key Industrial Catalysts

During the ATP-funded project, Catalytica and Microfluidics analyzed the catalysts used in the chemical and oil-refining markets. They made business/research contacts with 10 major chemical and catalyst manufacturers who agreed to perform much of the testing at their facilities, which would reduce internal staff and equipment costs for the Catalytica team. These potential customers were, at the same time, informal research collaborators. If successful, these customers would purchase the technology from Catalytica and Microfluidics. Together, they studied reactions to produce the following materials:

- Mixed metal oxide catalysts used for synthesizing chemicals, with a goal of five-percent yield improvement.
- Nanocrystalline zeolites used for catalytic cracking of petroleum to make gasoline components, with a goal of 25-percent productivity improvement.
- Colloidal-size catalysts used for residuum processing (residuum are the oil products that remain after petroleum has been distilled), with a goal of 10 cents/barrel cost reduction.
- Catalysts with controlled phase purity and reduced crystallite size for syngas manufacture. Syngas (or synthesis gas) is a mixture of carbon monoxide and hydrogen that is generated in coal gasification and some types of waste-to-energy facilities. Syngas is an intermediate step of natural gas to manufacture liquid fuels and other chemical products. Hydrogen is also produced from natural gas as an intermediate step in manufacturing basic chemicals.
- Catalyst support materials used to improve surface area and porosity (these included gamma alumina, diaspore, and a low thermal expansion ceramic precursor).

***A five-percent improvement in selectivity would reduce waste emissions by 10 million pounds per year and save several million dollars annually in raw materials and fuel costs.***

### Initial Results Are Limited

While Catalytica and Microfluidics developed the new reactor, they also continued working with each of the customer/research collaborators. Progress was difficult because of their customers' shifting priorities and deadlines.  Although some progress was made, customers decided to either pursue the work internally or abandon the technology. The results of their research to produce catalytic materials are described here:

- **Mixed metal oxide catalysts for synthesizing chemicals.** Catalytica and Microfluidics prepared formulations of copper-zinc-aluminum mixed oxides. They were able to improve the mixing, and the resulting crystallite sizes were significantly smaller, with improved phase purity. This was one of the major developments of the program, which provided incentive to pursue other catalyst systems. The team made two efforts with mixed metal oxides:
    - Together with one chemical company collaborator, they worked to improve control of precipitation. The new mixer/reactor provided no catalytic benefit. The company chose to pursue internal projects instead.
    - Together with a second chemical company, they worked to increase reaction rates through the use of fine-grained particles and further reduced the size with the new mixer/reactor. Preliminary results showed some difference in catalytic performance, but not dramatic improvements. The technology was incompatible with the collaborator's in-place synthesis methods, so the project was abandoned.
- **Nanocrystalline zeolites.** Hydrocracking is used to produce superior-quality, stable lubricants. The process works by reacting a petroleum feedstock with hydrogen, in the presence of a catalyst, at high temperatures (400-425°C) and pressures (3000+ psi [pounds per square inch]). The process eliminates impurities. The team made two efforts to perform hydrocracking with zeolites:
    - Together with one oil company, they worked to synthesize zeolite Y, which had a large potential market. Processing with the Microfluidizer increased the rate of high-quality, zeolite synthesis, but only marginally decreased crystallite size.

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The researchers achieved some enhancements in catalyst yield, but test product samples had limited reproducibility.

- Together with a catalyst manufacturer and a chemical company, their initial results showed significant stability advantages, although follow-up testing was less favorable. The chemical company discontinued the project.

- **Colloidal catalysts.** Catalytica and Microfluidics worked with another oil company to develop improvements in catalysts used in residuum processing. Researchers sought to provide “drop-in” catalyst replacements, but this effort was abandoned because margins for improvement were too small to be cost effective.

- **Syngas catalysts.** In principle, the smaller the crystallite size, the higher the activity of the catalyst. However, very small copper crystallites are unstable in syngas reactions. The team had to balance initial activity and long-term stability. They made two efforts in the area of syngas catalysts:

  - Together with one catalyst manufacturer, they created promising test materials with high catalyst stability.

  - Together with a chemical company, they evaluated the synthesis of copper-zinc-aluminum mixed oxide catalysts. They prepared a series of catalyst samples, and resulting materials showed superior activity maintenance. However, the chemical company ultimately decided to proceed with internal developments instead of pursuing the ATP-funded technology.

- **Catalyst supports**(diaspore and low thermal expansion ceramic precursors). These are fine white powdery substances with high fusing temperatures used in ceramic coatings.

  - The team reduced diaspore synthesis times from days to a few hours. Catalytica proposed to construct a continuous pilot-scale unit for a catalyst support manufacturer, but the manufacturer declined.

  - A small company wanted to develop specialty low-thermal-expansion ceramics as exhaust port liners for diesel engines. They needed a low-cost route to produce the material in 100-kilo quantities. Researchers investigated two compositions: one based on barium-zirconium-silicon phosphate and another based on calcium-strontium-zirconium phosphate. Ultimately, the effort was discontinued due to the extensive washing steps needed to purify the material.

By 1998, at the end of the ATP project, Catalytica and Micorfluidics had developed a prototype mixer reactor, called the Multiple Stream Mixer/Reactor (MMR), and used it with their customers/research partners. They received three patents for this technology and disseminated knowledge in several academic journals and presentations. The project continued for another year with approximately $350,000 of internal joint venture funding. However, without the financial backing of a large, full-time research team, they were unable to make the strides necessary to validate the technology. The researchers still believed that the basic premise of the project was valid: ultraturbulent mixing of two or more solutions would result in precipitation and increased homogeneous nucleation (the initial stage of precipitate formation) with a larger number of small crystallites of precipitate. However, they were unable to prove this during the project’s limited timeframe. Customers who manufactured catalysts were hesitant to outsource their research and development, and some of their existing synthesis methods proved to be incompatible with both the Microfluidizer and the new MMR. Catalytica (later renamed Catalytica Energy Systems) abandoned the technology in 1999, but Microfluidics continued.

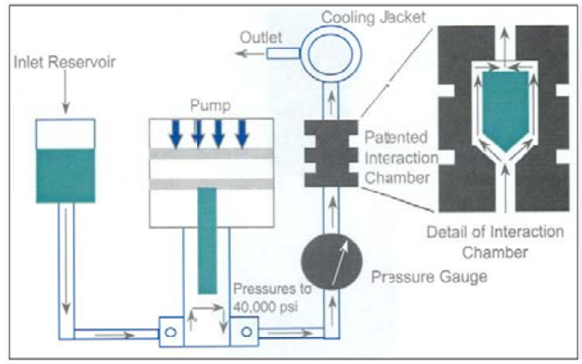
## MMR on the Brink of Success

Commercialization was difficult in a competitive, commodity environment, but Microfluidics (later a division of MFIC Corporation) continued to develop the MMR. After some delay due to internal business changes, the market began to express interest in their reactor. In 2003, the company performed testing for a biotechnology firm using the ATP-funded technology.

***Catalytica and Microfluidics had developed a prototype mixed reactor, called the Multple Stream Mixer/Reactor (MMR), and used it with their customers/research partners.***

MFIC introduced its patented MMR to the market in 2004 as a continuous chemical reactor (see illustrations below). Each solution feed stream reaches velocities of 80 to 300 meters per second. The two streams collide and combine efficiently in a patented reaction chamber. Increasing the level of supersaturation (higher than normal solute concentration dissolved in a solvent) through high-intensity mixing can result in an increased nucleation rate and a decrease in crystallite size of the precipitated product. In addition, intense mixing also increases homogeneity in pH and/or concentration. As a result, the properties of the product, in terms of phase purity, uniformity of composition, and uniformity of crystal size, are also improved. The MMR may become a standard device for conducting chemical reactions, especially to produce nanoparticles. This degree of reaction chemistry can reduce waste and lead to efficient manufacturing of new nano-structured materials in scalable quantities.

Irwin J. Gruverman, Chairman and CEO of MFIC, said, “[The MMR] permits creation of incredibly small structures that allow reactions to occur very rapidly at the nanometer scale, and that produce the smallest, most uniform and purest reaction products… [W]e can produce these nanomaterials quickly, phase-pure, and very uniform… We will enable new products, improve old products, and… revolutionize the way people do reaction chemistry…. The [MMR] advantages include much lower capital cost, because it is a continuous process unlike the batch processes normally used today to perform reaction chemistry.




Photograph and schematic of MFIC’s patented MMR System, which permits fast, controlled, continuous reaction chemistries. The MMR aids the development and manufacture of nanomaterials. Two streams of liquid enter the inlet, pass through high-shear microchannels (up to 40,000 psi), and collide in an intense energy field (see schematic). Resulting materials have uniquely small crystallite size, improved nano-scale homogeneity, and improved chemical purity

Our technology is more energy-efficient, is easier to control and facilitates making pure material with minimal contamination…. The higher operating pressure allows us to put much more energy into the stream and get more uniform, stable microemulsions and nanosuspensions.”

In addition to catalysts, potential applications for materials produced in the MMR include the following:

- **Pharmaceuticals.** Solids can be recrystallized, purified, and then dispersed as nano-suspensions in an injectable medium. Nebulized (liquid converted to a fine spray) inhalable drugs can be prepared with nanoparticles.
- **Superconductors.** Particle uniformity at the nanometer scale improves performance.
- **Photographic media.** Resolution and performance depend on crystalline component size and uniformity.

- **Planarization abrasives.** In semiconductor manufacturing, it is critical that deposition layers be free of defects. Abrasive crystals are used to process the underlying surfaces of semiconductor layers.

- **Pigment synthesis.** Paint quality (such as appearance and wear) depends on uniform particle pigment properties.

- **Ceramics.** Nanoparticles minimize thermal expansion (increase in size due to an increase in temperature) and maximize isotropic strength (uniform strength in all directions).

- **Ultrapure chemicals.** Chemicals are recrystallized more completely by ultraturbulent processing.

MFIC commercialized its first laboratory MMR system in 2004, and its first major production MMR system is scheduled for commercialization in 2005 or 2006. The MMR can be custom-built to meet research and production needs. The laboratory system has a capacity of 10 gallons per hour, and MFIC projects that production systems will have throughputs of 200 gallons per hour and higher. The company demonstrated the MMR at the Massachusetts Institute of Technology's Emerging Technology Conference in September 2004 as a technology "poised to make a dramatic impact on the world."

***MFIC introduced its patented Multiple Stream Mixer/Reactor to the market in 2004 as a continuous reactor.***

## Conclusion

Catalytica, Inc. (now Catalytica Energy Systems) and Microfluidics (now MFIC Corporation) formed a joint venture in 1994 to develop a comprehensive methodology to improve catalyst manufacturing. Catalysts are used to speed chemical reactions. More active catalysts could be used in the oil refinery and chemical manufacturing industries to increase energy efficiency and reduce waste in the manufacturing process.

The companies applied to ATP for cost-shared funding in 1994, and ATP awarded funding for a three-year project, beginning in 1995. The Catalytica team analyzed reactions for five types of catalysts, with some positive results. They used their knowledge to develop a new mixer/reactor, called a Multiple Stream Mixer/Reactor (MMR), which enabled fast, controlled, continuous reaction chemistries for smaller and purer product particles (nanometer scale, down to billionths of a meter). They received three patents for these advances and shared their results in academic journals and presentations. MFIC commercialized the MMR in 2004 for laboratory use and anticipates offering a manufacturing-scale model in 2005 or 2006. The resulting nanoparticles may be useful for many industries such as biotechnology, pharmaceuticals, cosmetics, chemicals, coatings, and electronics.

# PROJECT HIGHLIGHTS
## Catalytica Energy Systems (formerly Catalytica, Inc.)

**Project Title:** Development of Improved Catalysts Using Nanometer-Scale Technology

**Project:** To develop and demonstrate the manufacturability of catalysts with enhanced activity and selectivity for use in the chemical and petroleum-refining industries.

**Duration:** 1/16/1995–3/31/1998
**ATP Number:** 94-01-0190

**Funding(in thousands):**

| | | |
|---|---|---|
| ATP Final Cost | $1,994 | 47% |
| Participant Final Cost | 2,262 | 53% |
| Total | $4,256 | |

**Accomplishments:** While the ATP-funded project failed to meet its original goal to increase the productivity of catalysts in the chemical and petroleum-refining manufacturing processes, Catalytica and Microfluidics did make the following technical advances in enhancing catalyst production:

- Using the existing Microfluidizer equipment, improved the mixing, homogeneity, and phase purity; resultant catalyst crystallite sizes were significantly smaller.

- Developed a prototype mixer/reactor (Multiple Stream Mixer/Reactor [MMR]) by 1998 and began testing with customer/research partners. MMR allowed fast, controlled, continuous reaction chemistries. Resulting catalysts had uniquely small crystallite size, improved nano-scale homogeneity, and improved chemical purity.

- Produced an improved MMR, in which two solution streams enter, pass through high-shear microchannels under high pressure (up to 40,000 pounds per square inch), and collide in a unique reaction chamber.

Microfluidics was awarded three patents for this ATP-funded technology:

- “Use of multiple stream high pressure mixer/reactor”
(No. 6,159,442: filed August 5, 1998; granted December 12, 2000)

- "Multiple stream high pressure mixer/reactor”
(No. 6,221,332: filed August 5, 1998; granted April 24, 2001)

**Commercialization Status:** Microfluidics’ MMR may prove to be a valuable tool for the emerging nanotechnology sector, producing nanoparticles for many industries. The company sold its first laboratory MMR system in 2004 and expects the first major production MMR system to become available in 2005 or 2006.

**Outlook:** The outlook for MMR technology is good but clouded. Although Catalytica and Microfluidics found it difficult to enter the petroleum and chemical-refining markets, their research may benefit other industries. For example, the ultra-fine particles resulting from the MMR are potentially useful in cosmetics, pharmaceuticals, paints, and coatings.

**Composite Performance Score: * ***

**Numbers of Employees:** 120 employees at project start, 85 as of December 2000 (Catalytica); 40 employees at project start, 42 as of March 1998, and 47 as of December 2004 (MFIC Corporation).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## PROJECT HIGHLIGHTS
## Catalytica Energy Systems (formerly Catalytica, Inc.)

### Publications:

Catalytica and MFIC researchers disseminated their findings through the following publications:

- Moser, W. R., B.J. Marshik, J. Kingsley, M. Lemberger, R. Willette, A. Chan, J.E. Sunstrom IV, and A. Boyce. “The Synthesis and Characterization of Solid States Materials Produced by High Shear Hydrodynamics Cavitation.” Journal of Materials Research, Vol. 10: 2322-2335, 1995.

- Gruverman, I. J. “Production of Nanostructures under Ultraturbulent Collision Reaction Conditions – Applications to Catalysts, Superconductors, CMP Abrasives, Ceramics, and other Nanoparticles.” Mat. Res. Soc. Symposium Proceedings, Vol. 775, 2003.

- Gruverman, I. J. “Ultraturbulent Reaction Technology.” Drug Delivery Technology, Vol. 3, No. 1, January 2003.

### Presentations:

They also shared knowledge through the following presentations:

- Kilner, P. H. “Liquid Acid Replacement.” Solid Acid/Base Conference, Houston, TX, February 26-28, 1995.

- Moser, W. R., J. E. Sunstrom, and B. J. Marshik-Geurts. American Chemical Society, Anaheim, CA, April 4, 1995.

- Ginter, D. M., D. L. King, and P. H. Kilner. "Use of a High Intensity Multistream Mixer for the Precipitation of Catalyst Precursors Having Reduced Crystallite Size and Improved Phase Purity." American Institute of Chemical Engineers (AIChE), Miami Beach, FL, November 1998.

- Ginter, D. M., D. L. King, and P. H. Kilner. "Effect of a Novel Multistream Mixer/Reactor in Reducing Mass transfer Limitations in a Model Fast Chemical Reactions.” (AIChE, Miami Beach, FL, November 1998.

- Microfluidics demonstrated the MMR at the juried Massachusetts Institute of Technology’s Emerging Technology Conference as a technology “poised to make a dramatic impact on the world.” September 29-30, 2004.

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